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Effects of long storage in La-Sr manganites with pared divalent and quadrivalent substituents for manganese

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Abstract. The results of investigation on the ageing of ceramic manganites $La_{1-c}Sr_cMn_{0.90}Ni_{0.05}Ge_{0.05}O_{3+\gamma}$ and $La_{1-c}Sr_cMn_{0.90}Zn_{0.05}Ti_{0.05}O_{3+\gamma}$ (c = 0.15, 0.17, 0.19) during long-term storage at normal conditions are presented. Unit cell volume of all manganites having rhombohedral structure decreased over time. The width of X-ray diffraction reflexes from (Ni,Ge)-compositions varied irregularly within the measurement error, and the width of reflexes from (Zn,Ti)-contained manganites decreased significantly. Magnetization of all samples increased in the end of storage period. Curie point of compositions with $c \geq 0.17$ exhibited some trend of increase. Ageing leaded to the lowering of "metal-semiconductor" transition temperature in (Ni,Ge)-substituted manganites. (Zn,Ti)-contained compositions showed only semiconductor behavior in investigated temperature range from 100 to 300 K, and the changes of their magnetic parameters were most considerable. The increase in magnetization and Curie point reached 7.5 % and 11 %, respectively. Possible mechanisms of ageing in considered materials are discussed in terms of oxidation processes, formation of microinhomogeneities and relaxation of internal stresses.

1. Introduction

Stability of the main parameters of functional magnetic materials in relation to prolonged storage is one of the most important conditions for their use in devices of magnetic and spin electronics. Manganites claim to be a new class of functional materials for various technical applications using the phenomena of colossal magnetoresistance, giant magnetostriction, electrical switching, etc. [1,2]. However, despite the large number of developments and studies of perovskite-like manganites, the ageing processes in these materials are not still fully understood, and available information concerning the ageing of bulk ceramic manganites is meager.

It's clear that the fundamental cause of ageing is the transition of the system into energetically more favorable state because manganites synthesized at high temperature after cooling are not in a state of thermodynamic equilibrium under storage conditions.

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In [3,4] the data on changes in structural and electromagnetic characteristics of manganites of the systems $La_{1-c+x}Sr_{c-x}Mn_{1-x}Me^{2+}{}_xO_{3+\gamma}$ ($Me^{2+} = Zn^{2+}$, Ni^{2+}; c = 0.15, 0.17 0.19) and $La^{3+}{}_{0.8-x}Sr^{2+}{}_{0.2+x}Mn^{3+}{}_{0.8-x-2\gamma}Mn^{4+}{}_{0.2+2\gamma}Ti^{4+}{}_xO_{3+\gamma}$ ($0.025 \le x \le 0.150$) during long-term storage and after thermal cycling were reported.

Unit cell volume of all rhombohedral manganites by the end of the storage period decreased, that was associated with increasing oxygen content according to thermodynamical notions [5].Changes in magnetization and Curie point depended on the composition of the manganites, and in Ni- or Zn-substituted samples variations of magnetization were within the error of measurement.

The data obtained were explained by oxidation processes, rearrangement of the substituting ions and vacancies between crystal sublattices and formation of microinhomogeneities.

Combined substitution of divalent and quadrivalent ions can promote the ordering or spatial redistribution of cations, formation of clusters, segregations, inhomogeneities and modulated structures [6-9] with various crystallographic and magnetic parameters, that must influence the ageing processes.

Here, we present the results of investigations on the ageing of ceramic manganites $La_{1-c}Sr_cMn_{0.9}(Ni_{0.5}Ge_{0.5})_{0.1}O_{3+\gamma}$ for 51 months and $La_{1-c}Sr_cMn_{0.9}(Zn_{0.5}Ti_{0.5})_{0.1}O_{3+\gamma}$ for 36 months in normal conditions. The values of "c" (c = 0.15, 0.17, 0.19) were chosen near "orthorhombic-rhombohedral structure" boundary on the phase diagram of the $La^{3+}{}_{1-c}Sr^{2+}{}_cMn^{3+}{}_{1-c}Mn^{4+}{}_cO_3$ system [10].

2. Experimental

Manganites have been prepared by traditional ceramic processing in air. The final sintering step was performed at 1473 K for 10 h, and the samples were cooled in the furnace. More detailed procedures of the synthesis are described in [11].

Phase composition and cell parameters were determined at room temperature from X-ray powder diffraction patterns recorded on the diffractometer Shimadzu XRD-7000 in CuK_α radiation.

Magnetization per mass unit (σ) was measured by ballistic method in magnetic field of 5600 Oe. Curie point (T_c) was determined on the temperature dependence of magnetic permeability ($\mu(T)$) as the temperature corresponding to the maximum of $\left| d\mu(T)/dT \right|$.

Measurements of dc electrical resistivity (R) were performed using contacts of self-hardening organometallic compound containing 99 % silver.

3. Results and discussion

Studied samples in initial state and after ageing were rhombohedral. Unit cell volume (V) of all compositions decreased over time (table 1), that may be ascribed to the oxidizing of manganites.

Table 1. Unit cell volume of manganites $La_{1-c}Sr_cMn_{0.9}(Me^{2+}{}_{0.5}Me^{4+}{}_{0.5})_{0.1}O_{3+\gamma}$ in initial state (I) and in the end of storage period (II).

Composition		V (Å^3)	
(Me^{2+}, Me^{4+})	c	I	II
(Ni^{2+},Ge^{4+})	0.15	353.01	352.43
	0.17	352.56	352.37
	0.19	352.21	351.92
(Zn^{2+},Ti^{4+})	0.15	354.58	354.11
	0.17	354.35	354.07
	0.19	353.79	353.24

Oxidation causes the increase of the concentration of Mn^{4+} ions bonded with Mn^{3+} by double exchange interaction that leads to higher ferromagnetic characteristics and conductivity. On the contrary, the dilution of Mn sublattice by cation vacancies aggravate electromagnetic parameters.

Table 2. Magnetization at 80 K, Curie point and "metal-semiconductor" transition temperature (T_{ms}) of manganites $La_{1-c}Sr_cMn_{0.9}(Me^{2+}_{0.5}Me^{4+}_{0.5})_{0.1}O_{3+\gamma}$ in initial state (I) and in the end of storage period (II).

Composition		σ (emu/g)		T_c (K)		T_{ms} (K)	
(Me^{2+}, Me^{4+})	c	I	II	I	II	I	II
(Ni^{2+},Ge^{4+})	0.15	73.3	75.3	249	249	238	224
	0.17	75.1	76.2	238	247	220	217
	0.19	75.7	77.5	250	248	221	218
(Zn^{2+},Ti^{4+})	0.15	48.4	51.8	203	196	–	–
	0.17	45.0	48.4	185	193	–	–
	0.19	46.6	50.0	178	197	–	–

During storage period magnetization of all manganites and Curie point of the samples with c = 0.17, as well as T_c of (Zn,Ti)-substituted manganite with c = 0.19, increased (table 2). At the same time, the decline in magnetic permeability of these samples with increasing temperature became more protracted (figure 1a and figure 2), which indicates the occurrence of magnetic inhomogeneities. Maximum changes in magnetization and Curie points for (Ni,Ge) compositions were 3 % and 4 %, respectively, and for (Zn,Ti)-contained samples they reached 7.5 % and 11 %. The changes of electrical parameters were more significant.

All (Ni,Ge)-contained compositions exhibited some trend of "metal-semiconductor" transition temperature lowering (table 2). T_{ms} of the composition with c = 0.15 decreased by 14 K, and figure 1b illustrates qualitatively different kind of the temperature dependences of resistance of initial and aged samples. All (Zn,Ti)-substituted samples showed only semiconductor behavior in investigated temperature range from 100 to 300 K.

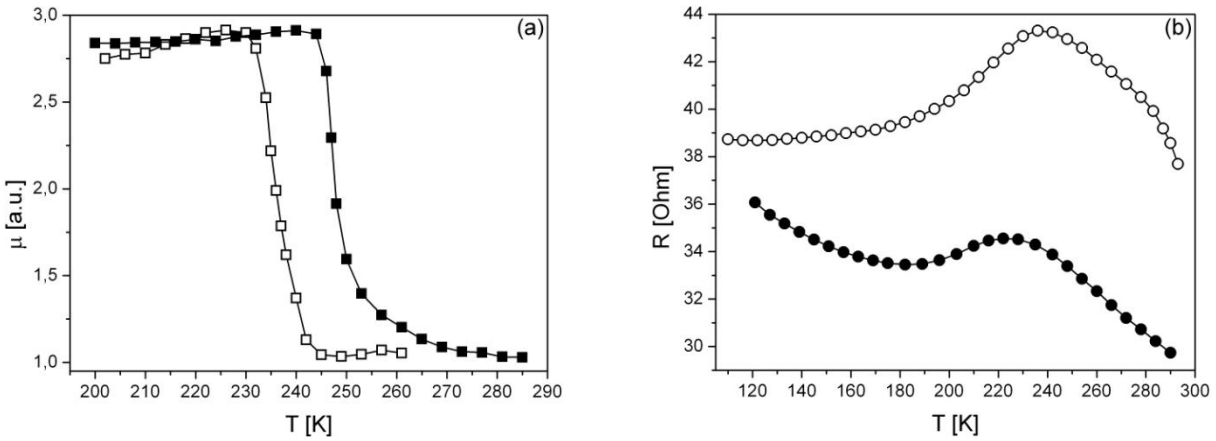

Figure 1. Temperature dependencies of magnetic permeability (a) and electrical resistance (b) of manganites $La_{1-c}Sr_cMn_{0.9}(Ni_{0.5}Ge_{0.5})_{0.1}O_{3+\gamma}$ in initial state (light symbols) and in the end of storage period (black symbols): (□,■) – c = 0.17; (○,●) – c = 0.15.

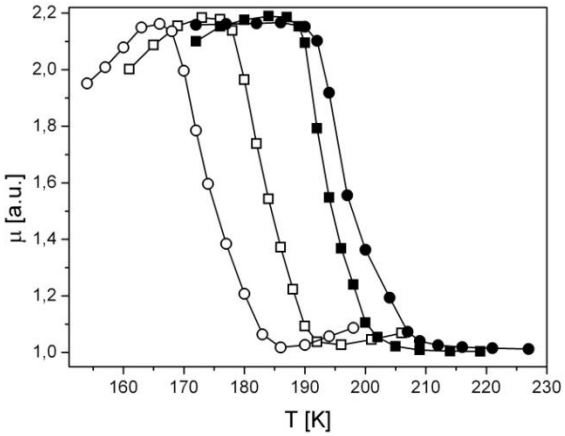

Figure 2. Temperature dependencies of magnetic permeability of manganites $La_{1-c}Sr_cMn_{0.9}(Zn_{0.5}Ti_{0.5})_{0.1}O_{3+\gamma}$ in initial state (light symbols) and in the end of storage period (black symbols): (□,■) – c = 0.17; (○,●) – c = 0.19.

Table 3. Full width at half maximum (FWHM) of diffraction reflexes of $La_{1-c}Sr_cMn_{0.9}(Me^{2+}_{0.5}Me^{4+}_{0.5})_{0.1}O_{3+\gamma}$ manganites in initial state (I) and in the end of storage period (II).

Composition		(HKL)	FWHM (°)	
(Me^{2+},Me^{4+})	c		I	II
	0.15	(102)	0.115	0.113
		(110)	0.119	0.122
		(116)	0.120	0.118
		(214)	0.108	0.112
		(208)	0.119	0.116
	0.17	(102)	0.110	0.109
		(110)	0.116	0.113
(Ni^{2+},Ge^{4+})		(116)	0.123	0.113
		(214)	0.107	0.110
		(208)	0.110	0.115
	0.19	(102)	0.110	0.112
		(110)	0.114	0.121
		(116)	0.133	0.131
		(214)	0.109	0.113
		(208)	0.116	0.121
	0.15	(102)	0.146	0.110
		(110)	0.154	0.130
		(116)	0.162	0.151
		(214)	0.174	0.127
		(208)	0.200	0.141
	0.17	(102)	0.150	0.109
		(110)	0.154	0.125
(Zn^{2+},Ti^{4+})		(116)	0.162	0.114
		(214)	0.166	0.138
		(208)	0.174	0.145
	0.19	(102)	0.128	0.113
		(110)	0.146	0.130
		(116)	0.183	0.119
		(214)	0.191	0.130
		(208)	0.209	0.145

Variations of X-ray diffraction reflexes width during the storage of manganites are presented in table 3. The width of reflexes from (Ni,Ge)-substituted manganites varied irregularly within the measurement error, and all reflexes from (Zn,Ti)-contained compositions narrowed significantly in the end of storage period. The narrowing of the reflexes at small angles indicates an increase in the size of coherent scattering regions, and at large angles it provide some evidence for the reduction of microstrains that could be associated with modulated structures [9].

The marked difference in the properties of (Ni,Ge)- and (Zn,Ti)-contained manganites is due to the fact that Zn^{2+} has the largest ionic radius among other ions in octahedral sublattice, the radius of Ge^{4+} ion is equal to the radius of Mn^{4+}, while Ti^{4+} has a radius significantly exceeding the radius of Mn^{4+} ion. Therefore, in (Zn,Ti)-substituted manganite microstresses and microstrains are higher than in (Ni,Ge)-contained samples.

4. Conclusion

From the results obtained, it might be concluded that the drift of structural and electromagnetic characteristics of considered manganites during prolonged storage can be related to oxidation processes, formation of microinhomogeneities and relaxation of elastic stresses. Considerable difference of radii and charges of Ni^{2+} and Ge^{4+}, Zn^{2+} and Ti^{4+} ions, Coulomb interaction promote redistribution of cations and vacancies in the volume of the crystals leading to separation of inhomogeneities.

Obviously, after cooling from the sintering temperature, the samples were in a thermodynamically nonequilibrium state. Transition to an energetically more favorable state should be accompanied by oxygen absorption [5,8], causing the transition $Mn^{3+} \rightarrow Mn^{4+}$ and leading to the formation of cation vacancies. As a result, unit cell volume of manganites decreases, and the concentration of ion pairs (Mn^{4+},Mn^{3+}) bonded by the double exchange interaction increases, which causes an increase in ferromagnetic characteristics. Competing factors are the reduction of the magnetic moment of manganese ions and dilution of the octahedral sublattice by vacancies. In addition, redistribution of cations on the vacant sites of the sublattices [5,8,12] is not excluded.

In the studied manganites with paired substitution of divalent and quadrivalent ions for manganese natural ageing processes are more pronounced than in monosubstituted manganites containing Ni, Zn or Ti.

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